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INTERNAL REPORT

SELECTIVE ISOTOPE DESORPTION

BY

Al Purer

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Branch of Applied Research

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ABSTRACT

This investigation covers the separation and concentration of isotopes of the light gases. Separation of the isotopes was achieved by a system based on one phase of the adsorption phenomena; that of desorption. The gases nitrogen, argon, neon, and helium were adsorbed at temperatures below their critical values on charcoal and then slowly desorbed at and above their critical temperature. Mass spectrometer analysis of the final product showed that isotope ratios of helium and neon could be significantly changed.

INTRODUCTION

This study represents preliminary work in evaluating the feasibility of the cryogenic chromatography project. The data obtained will be useful in establishing the experimental conditions of this investigation.

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It is also desirable to find if and to what extent selective isotope desorption can be obtained. If successful one could possibly outline a procedure that would allow the concentration of specific isotopes. For instance, helium-3 in Grade-A helium, being 0.1 part per million (1),^{2/}

^{2/} Underlined numbers in parentheses refer to references at the end of this report.

makes direct analysis difficult. Therefore, a concentrating system which would allow analysis by conventional mass spectrometry would be very desirable.

This report presents one method that may be useful in isotope concentration based upon selective isotope desorption. The gases nitrogen, argon, neon, and helium were desorbed from coconut-hull charcoal; the first part of the gas, the lighter isotope, was vented, leaving behind an enrichment of the heavier isotope. Analysis of the final product showed that the isotope ratio of helium and neon could be significantly changed. By staging the desorption process, one may be able to obtain a single isotope in a highly purified form.

APPARATUS AND EXPERIMENTAL PROCEDURE

The equipment used for this experiment consisted of a CEC 21-620A^{3/}

^{3/} References to names of specific equipment used are made to facilitate understanding and do not imply endorsement by the Bureau of Mines.

mass spectrometer operated with an ionizing current of 30 to 50 microamperes, a brass cell containing approximately one gram of coconut charcoal with a surface area of $1,700 \text{ m}^2/\text{g}$, an absolute pressure transducer, a recorder, a vacuum pump, a source of low temperature such as liquid nitrogen or liquid helium contained in a dewar flask, and a lab jack which was adjusted to obtain desired temperature. The general configuration of the above equipment is shown in figure 1.

The general experimental procedure followed for nitrogen, argon, neon, and helium consisted of first regenerating the charcoal by maintaining a vacuum of 0.1 mm Hg for a period of at least two hours at room temperature. The cell was then cooled to a temperature slightly below that of liquefaction for the gas under study. The sample gas was then allowed to enter the cell in an amount greater than that required to saturate the charcoal. The excess gas would liquefy with a vapor pressure of several hundred mm Hg. This vapor was pumped off, leaving charcoal saturated with the gas under study. The charcoal was next allowed to warm to a temperature which gave a pressure of 10 to 50 mm Hg vapor pressure. This temperature varied for different gases; for nitrogen, desorption started around 100° K ; argon, 110° K ; neon, 40° K ; and helium, approximately 15° K . This gas enriched in the lighter isotope was pumped off. The cell was then allowed to warm further and analyses were made on the remaining gas.

The method of analysis using the mass spectrometer consisted of running the desorbed sample at whatever pressure it came off the charcoal.

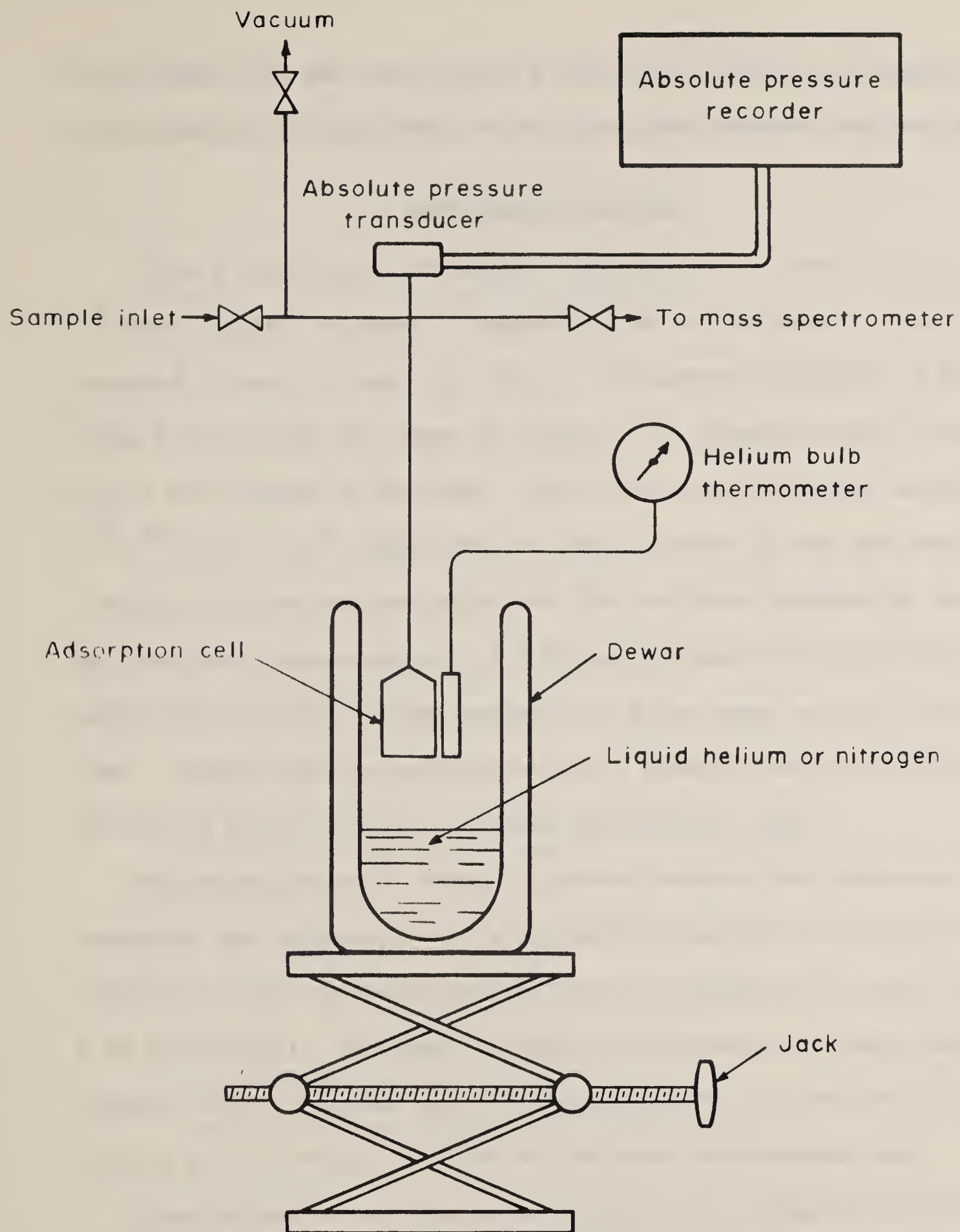


FIGURE 1. — Apparatus for Selective Isotope Desorption Studies.

The original gas was then run as a standard at the same pressure, thus standardizing the instrument at an equivalent pressure for each analysis.

EXPERIMENTAL RESULTS

From a theoretical standpoint, nitrogen is the most difficult gas of those studied to obtain a separation of its isotopes. If any change occurred it was too small to detect. The natural abundance of the N^{15} being 0.36 percent (2), made it difficult to determine small changes with a high degree of accuracy. Also, the mass difference in the diatomic $N^{14}-N^{14}$ and $N^{15}-N^{14}$, which are the two m/e peaks in the mass spectrometer used for calculations and which are the form that nitrogen is adsorbed and desorbed, represents only a 3.56 percent mass difference which indicates that the rates of desorption of the two gases would be about the same. Another problem encountered was a somewhat variable background for the m/e 28 and 29 peaks on the mass spectrometer scan.

Monoatomic argon⁴⁰, being 11 percent heavier than monoatomic argon³⁶, presented what appeared to be a favorable situation for selective isotope desorption until we considered the natural abundance of argon³⁶ which is 0.34 percent (2). This made it difficult to determine small changes in isotope ratios. Another problem encountered was the variable background for the m/e 36 and m/e 40 peaks on the mass spectrometer scan.

Neon offered a very favorable situation for selective isotope desorption with monoatomic Ne^{22} being 10 percent heavier than monoatomic Ne^{20} . This high mass difference should yield a significant difference in desorp-

tion rates. The natural abundance of Ne^{22} being 9.21 percent (2) made it easy to determine changes of isotope ratios by mass spectrometry. In this m/e 20-22 region the mass spectrometer did not suffer from the variable background that was found with the heavier gases.

In actual experimentation the first attempt gave an increase of 7.6 percent of the original Ne^{22} content. Later experiments showed a maximum of about 8.7 percent increase. In absolute value the Ne^{22} isotope was raised from its natural abundance of 9.21 percent to 10.1 percent.

The fourth gas studied was the He^3 - He^4 system. The He^3 content in normal helium is 0.1 ppm (1) which is too low to detect by mass spectrometry. Therefore, a synthetic helium mix containing 1.09 percent He^3 was obtained from the Mound Laboratory.^{4/} Helium, being an inert gas, would

^{4/} The Mound Laboratory is an Atomic Energy Commission facility at Miamisburg, Ohio. It is operated under contract by the Monsanto Chemical Company.

be adsorbed monoatomically which, with He^4 being 33 percent heavier than He^3 , represents a favorable system for selective isotope desorption. This experiment was done in the same manner as the other gases with the exception that a second stage of desorption was tried.

The first desorption decreased the He^3 content by about 14 percent of its original amount. The original 1.09 percent He^3 content was

reduced to 0.94 percent. This gas, after analysis, was readsorbed and redesorbed. This second stage of desorption decreased the He^3 content by about 18 percent from its starting point, 0.94 percent, with a final content of 0.77 percent. This showed that staging could be used to obtain a significant enrichment of the He^3 content in helium.

SUMMARY

The results of the experimentation described in this report show that it is possible to concentrate the isotopes of certain light gases by selective isotope desorption. The effectiveness of this method is shown for various gases in table 1. It should be possible to increase the efficiency by using a system which can take advantage of both adsorption and desorption such as a chromatographic column.

TABLE 1.-Effectiveness of selective isotope desorption

Isotope	Difference in Mass (Percent) ^{1/}	Original Concentration (Percent)	Final Concentration (Percent)	Change in Concentration (Percent)
N^{15}	3.6	0.36	0.36	0
Ar^{36}	10.0	0.34	0.34	0
Ne^{22}	9.1	9.21	10.1	8.7
He^3	33.0	1.09	0.94	14.0
He^3	33.0	0.94	0.77	17.0
<u>2/</u> He^3	33.0	1.09	0.77	29.0

^{1/} The heavier isotope taken as the denominator.

2/ Two-stage selective isotope desorption.

REFERENCES

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